

(19)



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(11)

EP 0 694 518 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
31.01.1996 Bulletin 1996/05

(51) Int. Cl.⁶: **C07C 41/09, C07C 43/04,
C07C 29/145, C07C 31/10**

(21) Application number: **95302800.8**

(22) Date of filing: **26.04.1995**

(84) Designated Contracting States:
DE FR GB

(30) Priority: **02.05.1994 US 236807**

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(54) Production of isopropyl alcohol and diisopropyl ether

(57) A two-step integrated process for the generation of diisopropyl ether from an acetone-containing stream comprises:

a) reducing the acetone-containing stream over a bulk metal, nickel-rich catalyst to give an isopropanol-rich effluent;

b) passing said isopropanol-rich intermediate directly to a second reactor, and

c) subjecting said isopropanol-rich intermediate to dehydration conditions in the presence of hydrogen and a strong acid zeolite catalyst from the group consisting of β -zeolite, β -zeolite modified with one or more metals from Groups IB and VIII of the Periodic Table, and a dealuminised Y-zeolite, optionally mixed with a binder selected from Group III or IV of the Periodic Table.

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Description

This invention concerns an integrated two-step method for the production of high octane blending components for reformulated gasoline such as diisopropyl ether (DIPE) from a crude low value acetone stream containing acetone, which method comprises (1) reducing the crude acetone stream in the presence of hydrogen over a reduction catalyst; and (2) feeding the isopropanol thus produced directly into a second reactor where the IPA is converted to DIPE over an acidic catalyst. If methanol (MeOH) or t-butyl alcohol (tBA) are also present in the feed, it is possible to produce methyl tertiary butyl ether (MTBE) or isopropyl tertiary butyl ether (IPTBE), respectively.

DIPE and IPTBE, as well as MTBE, are useful as octane enhancers in gasoline.

It is known to those skilled in the art that ethers, including both symmetrical and unsymmetrical ethers, may be prepared by reacting an alcohol with another alcohol to form the desired product. The reaction mixture, containing catalyst and/or condensing agent, may be separated and further treated to permit attainment of the desired product. Such further treatment commonly includes one or more distillation operations.

Of the ethers which can be produced, a great deal of attention has been directed toward the production of methyl tertiary butyl ether (MTBE) for use as a gasoline oxygenate.

U.S. Patent No. 4,918,244, to Nelson et al., discloses a method of preparing MTBE by continuously feeding t-butyl alcohol and methanol into a solid-acid catalyst bed, in a reactor separator rectification column in the presence of a solid acid catalyst, such as Amberlyst 15, whereby a product of substantially pure methyl tertiary butyl ether (MTBE) is separated from the reaction mixture.

Though MTBE is the most widely produced and discussed ether, other ethers are also being evaluated, such as diisopropyl (DIPE) and ethyl tertiary butyl ether (ETBE). DIPE can be produced from refinery propylene and water with isopropanol as an intermediate in this process. In a variation, isopropyl tertiary butyl ether could be produced by combining isobutylene with isopropanol.

The higher molecular weight ethers all have blending vapor pressures lower than MTBE, and much lower than ethanol. Their boiling temperatures are also higher than MTBE. Furthermore, higher molecular weight IPTBE has the potential to contribute more octane.

Although there has not been as much discussion regarding the production of IPTBE as there has been for MTBE, it is apparent that with its lower oxygen level and lower vapor pressure, there would appear to be a niche for IPTBE in the future of reformulated gasoline.

The β -zeolite catalysts found useful in this integrated process for production of IPA, DIPE, MTBE and IPTBE have been known in the art for some time. One of the earliest disclosures of zeolite beta was in U.S. Patent 3,308,069 (1967) to Wadlinger et al.

Patents in the art which employ zeolite beta relate mainly to dewaxing, and cracking of hydrocarbon feedstock.

An article entitled "Beta Zeolite as Catalyst or Catalyst Additive for the Production of Olefins During Cracking or Gas Oil," was written by L. Bonetto et al., 9th International Zeolite Conference, July 1992, FP 22. The authors note that with the greater demand for oxygenated compounds there is indication there might be increased demands for catalysts and conditions which maximize C_3 , C_4 and C_5 olefins. They suggest that β -zeolite could be used alone or combined with Y-zeolite as a suitable zeolite component. Various catalysts were studied with respect to minimization of diffusional requirements and zeolite stability.

In European Patent No 0 323 138 and U.S. Patent No 4,906,787, there is disclosed a catalytic process for converting light olefins to ethers suitable as high octane blending stocks carried out by contacting the olefin, especially propene, with water and alcohol recovered from a downstream distillation operation in an olefin conversion unit in the presence of an acidic zeolite catalyst. In this work diisopropyl ether (DIPE) was prepared from C_3H_6 and aqueous iso-PrOH in the presence of silica-bound zeolite Beta catalyst at 166°C.

In U.S. Patent No. 5,144,086, to Harandi et al., there is disclosed an integrated multistage process for the production of diisopropyl ether from substantially pure propene wherein in the second stage isopropanol containing about 0-20% water is contacted with an acidic large pore zeolite etherification catalyst which comprises a β -zeolite having a silica to alumina ratio of about 30:1 to 50:1.

In a European Patent No 0 323 268, light olefins are converted to alcohols and/or ethers in the presence of β -zeolite.

U.S. Patent No 4,058,576 to Chang et al. teaches the use of (pentasil-type) aluminosilicate zeolites, such as ZSM-5, having a pore size greater than 5 angstrom units and a silica-to-alumina ratio of at least 12, to convert lower alcohols to a mixture of ethers and olefins.

U.S. Patent No 5,225,609 to Bell discloses a process for the production of alkyl tertiary alkyl ether employing a zeolite catalyst, particularly zeolite beta which is pretreated either by steaming or hydrothermal treatment using liquid water at elevated temperatures. This process is claimed to be particularly effective in reducing the formation of dimethyl ether by product in the zeolite Beta catalyzed process for the formation of methyl tertiary butyl ether (MTBE) with high selectivity.

The use of faujasite zeolites in alkyl ether formation is also known in the art. The following references discuss the

use of faujasite zeolites in various applications.

In allowed U. S. Patent 5,214,217, to T xaco Chemical Company, there is disclosed a method for preparing methyl tertiary butyl ether by reacting butanol and methanol in the presence of a catalyst comprising a super-acid alumina or a faujasite-type zeolite.

In U.S. Patent No. 3,955,939, to Sommer et al. (1976), there is disclosed the production of a water-free mixture of isopropyl alcohol, diisopropyl alcohol, diisopropyl ether and by-products by the catalytic hydration of propylene in the gaseous phase at temperatures of 140°-170°C, in the presence of a catalyst comprising a super-acid alumina or a faujasite-type zeolite.

It is also known to produce IPA and DIPE by the hydration of propylene and subsequent dehydration of IPA to DIPE.

In U.S. Patent No. 5,208,387, also to Harandi et al., there is disclosed a process for the acid catalyzed production of DIPE from propene and water feed stream that eliminates the propene recycle stream to the olefin hydration reactor and achieves high propene conversion. This process is carried out in two stages wherein the first stage comprises a zeolite catalyzed hydration and etherification of propene employing a minimum of water feed and the second stage converts unconverted propene from the first stage reactor by hydration and etherification to DIPE.

In the Applicant's related copending European Patent Application No. 94309912.7 there is disclosed a two-step process for generation of isopropyl t-butyl ether from crude acetone.

In the Applicant's related copending European Patent Application No. 94308188.5 there is disclosed a two-step process for the generation of diisopropyl ether from a crude by-product acetone stream which comprises hydrogenating said crude acetone over a bulk metal, nickel-rich catalyst to give an isopropanol effluent and subjecting said isopropanol-rich intermediate to dehydration conditions in the presence of a strong acid zeolite catalyst. This process requires interstage separation of the hydrogen prior to the dehydration step.

It does not appear that there is any disclosure or suggestion in the art of converting acetone to ethers in an integrated process. The portion of said by-product stream which typically comprises acetone is about 20% to 80%. The by-product acetone stream may also contain greater than 5% of both methanol (MeOH) and t-butanol (tBA). It would greatly enhance the economics of any process to produce MTBE or other oxygenates if acetone, along with some methanol and t-butanol, from a by-product stream could be converted to oxygenates such as DIPE, IPTBE and MTBE.

In a first aspect, the invention is a method for the generation of diisopropyl ether from an acetone stream, the method being an integrated process which comprises:

(1) reducing the acetone-containing stream in the presence of hydrogen and a reduction catalyst, and

(2) feeding the reduced isopropanol directly into a second reactor and reacting it in the presence of a strong acid zeolite catalyst from the group consisting of β -zeolite, dealuminised Y-zeolite, and metal-modified β -zeolite, optionally in combination with an oxide binder selected from Group III or IV of the Periodic Table.

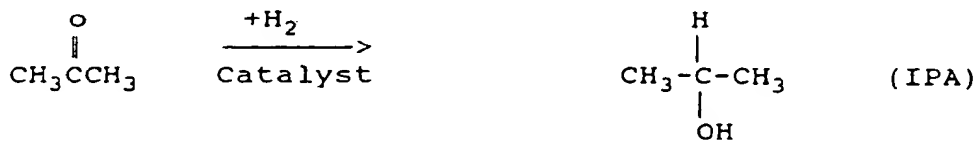
In a process to make propylene oxide, a large number of by-products are typically generated with the desired product. The by-products may include formic acid, acetic acid, their ester derivatives, t-butanol and acetone. The acetone may constitute about 20% to 80% of certain crude by-product streams. These crude acetone streams may be further mixed with methanol.

Copending European Patent Application No. 94309912.7 discloses a two-step process for generation of DIPE which requires interstage separation of hydrogen. Removal of hydrogen can cause propylene to oligomerize in the etherification reactor. In a commercial process this can greatly increase costs for purification of the DIPE product and regeneration of the catalyst.

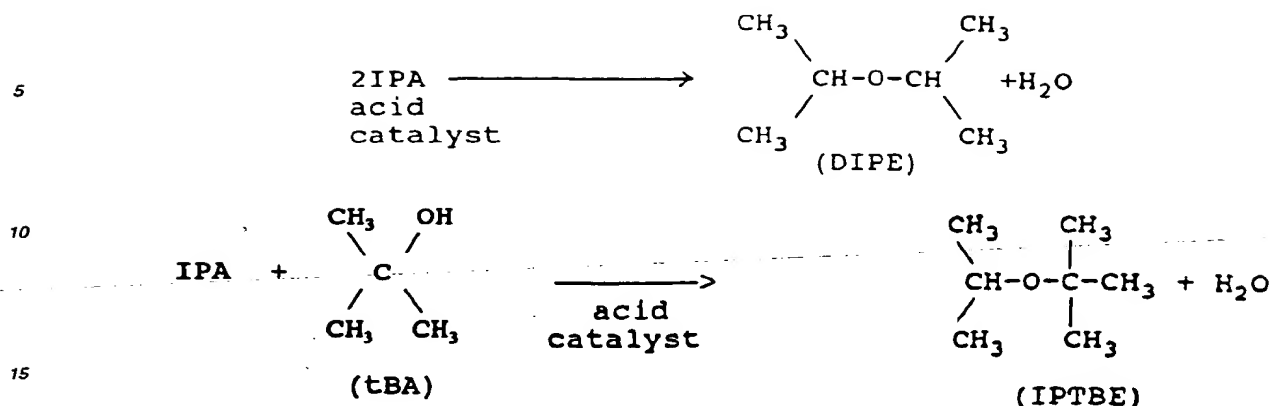
The instant invention provides an integrated process for the production of isopropyl alcohol and diisopropyl ether (DIPE), as well as methyl tertiary butyl ether (MTBE) and isopropyl tertiary butyl ether (IPTBE) where the crude acetone stream also contains methanol and t-butyl alcohol. For the generation of each of these oxygenates respectively the crude acetone should contain 10 - 40% each of methanol and t-butanol.

The integrated synthesis can be represented by:

Step I



Step II



In the first step the crude acetone stream is passed over a nickel-rich catalyst. The total metals loading of the catalyst is the range of 28 to 40 wt% of the support. The support material could be either one of the alumina, zirconia-alumina, titania-alumina and zeolite-alumina. The support comprises greater than 80% alumina and less than 20% of the other metal oxides. The preferred support for the catalyst used in the first step is alumina. A preferred nickel catalyst is characterized by having the composition, calculated in mol%, of from about 60%-99% nickel, and 1%-40% copper with the preferred proportions being about 65%-88% nickel, and 12%-35% copper. The temperature necessary to achieve the desired acetone hydrogenation to isopropanol (IPA) is 50-200°C, the preferred range is 100°-150°C.

The conversion of acetone to isopropanol in the first step is normally >90% per pass in continuous processing and in some instances it is at least as great as 99%.

In contrast to previous disclosures where a fractionation step is required after the hydrogenation of the acetone, the instant invention provides an improvement in that the alcohol-rich effluent from the first reactor goes directly to a second reactor without separation of the liquid and gas.

In addition to saving the cost of fractionation, a potential benefit is the complete removal of any peroxides such as di-t-butyl peroxide present in the crude acetone stream, which is a poison to acidic catalysts.

In the second reactor the alcohols can be etherified to ethers over an acidic catalyst, such as, for example, β -zeolite, ZSM-5, or Y-zeolite in the presence of hydrogen. The ether-rich effluent can subsequently be fractionated to isolate the ethers, such as, for example, DIPE, MTBE, and IPTBE for use as octane enhancers.

The zeolite can optionally be impregnated with a Group IB or VIII metal, including, but not limited to nickel and copper. This is demonstrated in Examples 1 and 2. In another embodiment, the metals can be deposited on a zeolite in combination with an oxide of Group III or IV of the Periodic Table. This is demonstrated in Examples 3 and 4.

The composition of zeolite beta is typically described as follows:

Zeolite beta is a crystalline aluminosilicate having a pore size greater than 5 Angstroms. The composition of the zeolite, in its as synthesized form may be expressed as follows:



where X is less than 1, preferably less than 0.7; TEA represents the tetraethylammonium ion; Y is greater than 5 but less than 100; and W is up to about 60 (it has been found that the degree of hydration may be higher than originally determined, where W was defined as being up to 4), depending on the degree of hydration and the metal cation present. The TEA component is calculated by differences from the analyzed value of sodium and the theoretical cation to structural aluminum ratio of unity.

Zeolite beta has two types of three-dimensional pore openings, the linear and the tortuous channel. The former has pore openings of 7.5Å x 5.7Å and the latter has pore openings of 6.5Å x 5.6Å. When silica, for example, is deposited on zeolite beta, the pore opening was narrowed or blocked by the deposited silica. It was concluded that silica deposition selectively removes strong acid sites and increases the population of medium acid sites.

In the fully base-exchanged form, zeolite beta has the composition:



where X, Y and W have the values listed above and n is the valence of the metal M. This form of the zeolite may be converted partly to the hydrogen form by calcination, e.g. at 200°C to 900°C or higher. The completely hydrogen form may be made by ammonium exchange followed by calcination in air or an inert atmosphere such as nitrogen.

The preferred forms of zeolite beta are the highly acidic, high silica forms, having silica-to-alumina mole ratio of at

least 10:1, and preferably in the range of 10:1 to 50:1 in the as-synthesized form, and a surface area of at least 100 m²/g.

Suitable β -zeolites for the practice of this invention include Valfor C806 β , Valfor CP815 β and Valfor C861. Valfor® is the registered trademark of the PQ Corporation.

Valfor® C806 β zeolite is zeolite beta powder in templating form. It is a high silica shape selective zeolite which contains the organic template used in the crystallization step, having been isolated after filtration and washing of the synthesis product. C806 β has a SiO₂/Al₂O₃ molar ratio of 23-26; the crystal size is 0.1-0.7 μ m; the surface area after calcination is about 700-750 m²/g; the cyclohexane adsorption capacity after calcination is 19-24g/100g; Na₂O content is about 0.01-1.0% by weight anhydrous; and, the organic content is about 11-13% by weight, on a water-free basis.

Valfor® C815 β zeolite is a calcined zeolite beta powder in hydrogen, sodium form. It is similar to C806 β except the product has been calcined to decompose the organic template. C815 β is a high silica, shape selective aluminosilicate with a large pore diameter. C815 β also has a SiO₂/Al₂O₃ molar ratio of about 23-26; the crystal size, surface area, cyclohexane adsorption capacity and Na₂O are all within the same ranges as given for C806 β .

Valfor® C861 β is an extrudate made of 80% C815 β powder and 20% alumina powder.

Y-zeolites are also useful and are from the group of faujasite zeolites. The unit cells of faujasite zeolites are cubic, $a_0 \approx 2.5$ nm, and each contains 192 silicon- or aluminum-centered oxygen tetrahedra which are linked through shared oxygen atoms. Because of the net negative charge on each of the aluminum-centered tetrahedra, each unit cell contains an equivalent number of charge-balancing cations. These are exclusively sodium ions in zeolites in their synthesized form. Typical cell contents for the Y-zeolites in the hydrated form are:



Y-zeolites are distinguished on the basis of the relative concentration of silicon and aluminum atoms and the consequent effects on detailed structure and related chemical and physical properties. The aluminum atoms in the unit cell of Y-zeolite vary from 76 to 48, resulting in a Si:Al ratio between 1.5 and 3.0. Both the cation concentration and charge density on the aluminosilicate structure are lower for Y-zeolites than for X-zeolites, where the aluminum atoms in the unit cell vary from 96 to 77.

Y-zeolites are particularly effective in the dealuminised form. Preferably, said Y-zeolites are dealuminised by ammonium exchange followed by calcination, or by treatment with ethylenediaminetetraacetic acid (EDTA) or other chelating agents or by treatment with fluorine or a fluorine-containing compound such as silicon tetrafluoride or ammonium fluorosilicate, or hydrothermal treatment and/or acid treatment. Said dealuminised Y-zeolites should have a silica-to-alumina molar ratio of greater than three, preferably a ratio of 5 or greater and most preferably a silica-to-alumina ratio of 5 to 100. The examples demonstrate the usefulness of catalysts having a silica-to-alumina ratio of 5 to 25 and particularly 5 to 10.

Examples of suitable commercially available dealuminised Y-zeolites include UOP's LZY-82 and LZY-72, PQ Corporation's CP-304-37 and CP-316-26, UOP's Y-85, Y-84, LZ-10 and LZ-210.

The unit cell size and SiO₂/Al₂O₃ molar ratio for typical dealuminised Y-zeolites are noted in the following table:

ZEOLITE TYPE	UNIT CELL SIZE, Å	SiO ₂ /Al ₂ O ₃ MOLAR
LZY-82	24.53	7.8
LZY-85	24.49	9.1
LZY-10	24.32	23.7
LZY-20	24.35	18.9
LZY-84	24.51	8.4
LZ-210	24.47	9.9
LZY-72	24.52	8.1
CP316-26	24.26	45.7

Said catalysts may be formed in the presence of a binder, such as Group III or Group IV oxide. Group III or Group IV oxides used in conjunction with said β -zeolite include oxides of aluminum, silicon, and titanium, zirconium, as well as combinations thereof. Alumina is preferred. Said binders may comprise 10% to 90% of the formed catalyst.

Particularly effective in the subject integrated production of DIPE, MTBE and IPTBE are the β -zeolites, optionally bound to an oxide, modified with multiple metals.

The metals useful for modifying the zeolite in the instant invention comprise those from Groups IB and VIII of the Periodic Table. Preferred metals are those found in Groups IB and VIII of the Periodic Table and include copper, nickel, palladium and platinum. Especially good results were observed using combinations of nickel and copper on a β -zeolite

in combination with alumina.

Said zeolites are preferably impregnated with said specified metals as their salts, particularly their metal nitrate or chloride salts, in an aqueous, alcoholic, or ketonic media over a period of 1-24 hours, then the solids are dried at elevated temperature, e.g. 120°C, for a period of time and calcined at 300-800°C for a further period, e.g. 315°C for 2 hours, followed by 540°C for another 2 hours, then reduced in a stream of hydrogen at $\geq 200^\circ\text{C}$.

The amount of the various metals deposited on the zeolite can vary. The amount of each individual metal, i.e., copper, nickel, palladium and platinum can vary from 0.01 to 10.0%. Where copper and nickel are deposited on zeolite/alumina extrudates the preferred weight percent is from 0.1% to 5.0%.

Said catalysts may be in the form of powders, pellets, granules, spheres, shapes and extrudates. The examples described herein demonstrate the usage of granules.

The process of the instant invention is carried out in two reactors in a series. The hydrogenation reaction of crude acetone stream is performed in a liquid phase downflow or upflow fixed bed reactor. The hydrogenation catalyst could be packed (loaded) into one, or more than one, zone with a quench zone in between the catalyst zones. The heat evolved from the hydrogenation reaction could be effectively removed by the quench stream in order to better control the reactor temperature. The etherification reaction could be conducted in either a fixed bed reactor or a catalytic distillation column.

Dehydration to the oxygenates can generally be conducted at temperatures from 20° to 250°C; the preferred range is 80° to 200°C. Good results are observed throughout this temperature range. However, it can be noted that the best conversion figures for MTBE, DIPE and IPTBE cogeneration are observed when the temperature is 120°-180°C. The total operating pressure may be from 0.1 to 14MPa, or higher. The preferred pressure range is 0.7 to 7MPa.

Typically, DIPE is generated continuously in up to ca. 30 wt% concentration or greater in the crude liquid product at total liquid hourly space velocities (LHSV) of 0.1 - 10/hour and relatively mild conditions, where:

$$\text{LHSV} = \frac{\text{Volume Of Total Liquid Feed Run Into The Reactor Per Hour}}{\text{Volume of Catalyst In Reactor}}$$

It is anticipated that MTBE and IPTBE can be generated in up to 20 or 15 wt% concentration or greater, respectively.

Conversions of isopropanol (IPA) are estimated in the following examples using the equation:

$$\frac{(\text{Mole\% of IPA in Feed} - \text{Mole\% of IPA in Product})}{\text{Mole\% of IPA in Feed}} \times 100$$

The examples which follow illustrate the integrated process for the synthesis of DIPE, and optionally IPTBE and MTBE, from a pure acetone feed, and optionally a crude acetone stream containing Acetone, TBA, MeOH, using β -zeolites, optionally modified with multiple metals, wherein the β -zeolites are optionally bound with an oxide.

The following examples specifically demonstrate:

- Although 35.8 wt% DIPE is obtained in Example 7, run 6013-700 using 32% Ni/Cu on Al_2O_3 in the top bed and 32% 60/40 Beta/ Al_2O_3 in the bottom bed, there is also 9.2 wt% gas produced.
- The overall best results might be typified by Example 5, Cut No. 6012-700 using the same top bed catalyst with 32% Ni/Cu on 80/20 Beta/ Al_2O_3 on the bottom. Here the wt% of DIPE is 30.0, however the wt% of undesirable gas is reduced to 4.6.

Catalyst screening runs were performed in a microreactor test unit which has two reactors in series separated by a quench zone. The reactors were operated in a downflow configuration. The top reactor was loaded with a 4 cm³ catalyst. The second reactor has two catalyst beds of 4cm³ of catalyst each separated by a 4 cm³ bed of inert material. The total charge of catalyst was 12 cm³ in the unit. Internal thermocouples were positioned at the bottom of each catalyst bed and at the inlet to the first reactor. The liquid feed was charged to the unit using a high pressure pump and the hydrogen was metered through a mass flow controller. For the purpose of simplifying the analysis of liquid products by GC, pure acetone (technical grade, 97%) was used as a feedstock to demonstrate the chemistry involved in the instant invention.

The catalysts were activated by heating slowly from room temperature to 260°C over a 6 hour period under flowing nitrogen at 0.5 MPa. The unit pressure was then raised to 3.5 MPa with hydrogen and the catalyst bed was held at 260°C for 10 hours under flowing hydrogen. The catalyst bed was cooled down to below 95°C. The acetone feed was charged to the unit at 1 LHSV based on total catalyst volume. The hydrogen flow rate can range from 1:1 - 10:1, however it was controlled to give a hydrogen to acetone mole ratio of 5:1 and a total pressure of 3.5 MPa. The acetone feed was mixed with hydrogen and preheated to 105°C. It was then fed into the first reactor which contained the hydrogenation catalyst. The first reactor was operated adiabatically. The hydrogenated feed left the first reactor and entered the second reactor. The reaction temperature in the second reactor was varied from 115°C to 149°C. The liquid product was collected periodically in a chilled receiver at -18°C and 2.1 MPa. The product was analyzed by GC to determine the composition of hydrocarbon and oxygenates, and by Karl-Fischer titration for the water content.

Preparation of Catalysts**Example 1**

5 A 92 g batch of alumina support was impregnated with 68 cm³ of an aqueous solution containing 94g of nickel nitrate hexahydrate and 9.9 g of copper nitrate hemipentahydrate. The impregnated support was dried at 121°C for 16 hours, and then calcined at 315°C for 4 hours. The calcined support was impregnated again with 68 cm³ of an aqueous solution containing 94g of nickel nitrate hexahydrate and 9.9g of copper nitrate hemipentahydrate. The impregnated support was dried at 121°C for 16 hours, and then calcined at 315°C for 4 hours and 482°C for 8 hours. The finished catalyst is Example 1.

EXAMPLE 2

15 A 50g batch of 80% β -zeolite/20% alumina support was impregnated with 41 cm³ of an aqueous solution containing 51g of nickel nitrate hexahydrate and 5.4g of copper nitrate hemipentahydrate. The impregnated support was dried at 121°C for 2 hours, and then calcined at 315°C for 4 hours. The calcined support was impregnated again with 73 cm³ of an aqueous solution containing 51g of nickel nitrate hexahydrate and 5.4g of copper nitrate hemipentahydrate. The impregnated support was dried at 121°C for 2 hours, and then calcined at 482°C for 8 hours. The finished catalyst is Example 2.

EXAMPLE 3

20 A 100g batch of 30% β -zeolite/70% alumina support was impregnated with a 80cm³ aqueous solution containing 102g of nickel nitrate hexahydrate and 10.8g of copper nitrate hemipentahydrate. The impregnated support was dried at 250°F/2 hours, and then calcined at 600°F/4 hours. The calcined support was impregnated again with a 73cm³ aqueous solution containing 102g of nickel nitrate hexahydrate and 10.8g of copper nitrate hemipentahydrate. The impregnated support was dried at 250°F/2 hours, and then calcined at 900°F/8 hours. The finished catalyst is Example 3.

EXAMPLE 4

30 A 1011g batch of Catapal B alumina powder was mixed with 3989g β -zeolite powder to make a 60/40 wt% mix based on dry powders. An aqueous solution containing 9.17g conc. nitric acid and 2128g water was prepared and added to the alumina/zeolite mix. An additional 214g of water was added. The paste was mix/mulled then extruded to normal 1.6 mm extrudates using a 2-inch screw extruder. The extrudates were dried at 110°C overnight.

EXAMPLE 5

35 Example 5 is an example of the invention. The catalyst from Example 1 was loaded in the top reactor and the catalyst from Example 2 was loaded in the bottom reactor. The Catalyst Evaluation Procedure described above was used. The results for this example are given in Table I. Under the test conditions, almost complete conversion of acetone was achieved. IPA and DIPE are cogenerated as the desired reaction products with high yields. Very small amounts of undesired propylene products are formed by the dehydration reaction of IPA. The DIPE yields increase with increasing temperatures of the etherification reactor (bottom reactor).

TABLE I - Results of Catalyst Evaluations

Example 5: Top Bed - 32% Ni/Cu on Al2O3
 Bot. Bed - 32% Ni/Cu on 80/20 Beta/Al2O3

GC Analysis of Liquid Product

Cut No.	TOS hr.	Avg. Top Temp. °C	Avg. Bot. Temp. °C	Liq. Recov. wt%	C3 wt%	Acetone wt%	IPA wt%	DIPE wt%	Water wt%	Gas wt%
6012-600	9	115	126	98.6	0.3	0.6	83.9	8.7	4.8	1.4
6012-700	20	118	137	95.4	0.5	0.5	54.3	30.0	10.0	4.6

EXAMPLE 6

Example 6 is an example of the invention. The catalyst from Example 1 was loaded in the top reactor and the catalyst from Example 3 was loaded in the bottom reactor. The Catalyst Evaluation Procedure described above was used. The results for this example are given in Table II. This example is used to illustrate the effect of β -zeolite content or catalyst acidity on the DIPE yield. Example 6 appears to exhibit a small advantage in DIPE yield over Example 5 at lower etherification reactor temperature, however, at higher temperature it does not give any advantage. As the space velocity was raised from 1 to 2 while maintaining the etherification reactor constant temperature, IPA yield increased and DIPE yield decreased. The results imply that Example 6 does not have sufficient acidic sites to convert the IPA to DIPE at the higher space velocity.

TABLE II - Results of Catalyst Evaluations

Example 6: Top Bed - 32% Ni/Cu on Al2O3
 Bot. Bed - 32% Ni/Cu on 30/70 Beta/Al2O3

GC Analysis of Liquid Product

Cut No.	TOS hr.	Avg. Top Temp. °C	Avg. Bot. Temp. °C	Liq. Recov. wt%	C3 wt%	Acetone wt%	IPA wt%	DIPE wt%	Water wt%	Gas wt%
6013-500	9 ⁺	115	127	100.0	0.0	0.0	82.9	12.2	4.9	0.0
6013-600	14 ⁺	115	135	94.7	0.3	0.5	64.1	25.2	4.6	5.3
6013-700	22 [*]	150	126	100.0	0.0	0.0	90.4	4.7	4.9	0.0
6013-800	30 [*]	151	134	96.0	0.3	0.5	74.3	16.2	4.7	4.0

* LHSV = 2;
 + LHSV = 1

EXAMPLE 7

Example 7 is an example of the invention. The catalyst from Example 1 was loaded in the top reactor and the catalyst from Example 4 was loaded in the bottom reactor. The Catalyst Evaluation Procedure described above was used. The results for this example are given in Table III. This example illustrates that optimum yields of DIPE can be attained by adjusting the zeolite content and etherification reactor temperature. DIPE yields of up to 35.8% were achieved by using the catalyst containing 60% β -zeolite and reaction temperature about 146°C. Etherification temperature greater than 146°C causes a deleterious effect on the combined IPA and DIPE yield because it favors the formation of undesired gas product.

The results from Examples 5, 6 and 7 clearly demonstrate that a high yield of IPA and DIPE can be generated from an integrated process where acetone is hydrogenated over a alumina supported Ni/Cu hydrogenation catalyst and the resulting IPA is dehydrated to ether over an acidic catalyst consisting of a β -zeolite/alumina support with or without additional hydrogenation function.

TABLE III - Results of Catalyst Evaluations

Example 7: Top Bed - 32% Ni/Cu on Al2O3
 Bot. Bed - 60/40 Beta/Al2O3

GC Analysis of Liquid Product

Cut No.	TOS hr.	Avg. Top Temp. °C	Avg. Bot. Temp. °C	Liq. Recov. wt%	C3 wt%	Acetone wt%	IPA wt%	DIPE wt%	Water wt%	Gas wt%
6014-500	5	116	117	100.0	0.0	0.0	90.5	4.6	4.9	0.0
6014-600	9	117	135	95.8	0.3	0.0	66.1	24.7	4.7	4.2
6014-700	17	118	146	90.8	0.3	0.0	50.3	35.8	4.5	9.2
6014-800	19	119	147	81.1	0.8	0.0	43.1	33.2	4.0	18.9

Claims

1. An integrated process for the generation of diisopropyl ether from an acetone-containing stream, which method comprises:
 - a) reducing the acetone-containing stream over a supported, hydrogenation catalyst to give an isopropanol-rich effluent;
 - b) passing said isopropanol without separation of liquid and gas directly to a second reactor and therein reacting said isopropanol in the presence of a strong acid zeolite catalyst from the group consisting of β -zeolite, β -zeolite modified with one or more metals from Groups IB and VIII of the Periodic Table and dealuminised Y-zeolite, optionally mixed with a binder selected from oxides of Group III or IV elements of the Periodic Table.
2. A process as claimed in Claim 1 wherein the supported hydrogenation catalyst comprises 16-28 wt% nickel and 5-16 wt% Cu on a support selected from Group III or IV of the Periodic Table.
3. A process as claimed in Claim 1 or claim 2 wherein the β -zeolite has a silica:alumina molar ratio of at least 10:1.
4. A process as claimed in any preceding claim wherein the zeolite catalyst is a β -zeolite formed in the presence of a binder selected from a Group III oxide or a Group IV oxide.
5. A process as claimed in claim 4 wherein the Group III oxide binder is alumina.
6. A process as claimed in any one of claims 1 to 3 wherein the zeolite catalyst is a zeolite, β -zeolite modified with one or more metals from Groups IB and VIII of the Periodic Table.
7. A process as claimed in claim 6 wherein the β -zeolite is modified with one or more metals selected from the group consisting of copper, nickel, palladium and platinum.
8. A process as claimed in claim 6 or claim 7 wherein the concentrations of metals deposited on said zeolite may vary from 0.01% to 10.0% for each metal.
9. A process as claimed in any one of claims 1 to 3 wherein the zeolite catalyst is a Y-zeolite dealuminised in a manner selected from:
 - a) ammonium exchanging the Y-zeolite followed by calcinating;
 - b) treating the Y-zeolite with ethylenediaminetetraacetic acid.
 - c) treating the Y-zeolite with a fluorine-containing compound from the group consisting of silicon tetrafluoride and ammonium fluorosilicate; or
 - d) treating the Y-zeolite with steam alone or followed by acid treatment.
10. A process as claimed in any preceding claim wherein the crude by-product acetone stream contains 20% to 80% acetone.
11. A process as claimed in any preceding claim wherein the acetone is hydrogenated in the first stage in the temperature range 120°-180°C.
12. A process as claimed in any preceding claim wherein the second stage generation of ether is conducted in the temperature range 800 to 200°C.
13. A process as claimed in any preceding claim wherein said acetone stream also contains significant quantities of methanol and/or t-butanol so that methyl t-butyl ether and/or isopropyl tertiary butyl ether are also produced.